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(54) Title: POLYMERIC MATERIAL AND CLEAR FILM PRODUCED THEREFROM

### (57) Abstract

The present invention is directed to a novel polymer which in one embodiment, was formed by extruding an admixture (either a physical blend of solids, or a compounded melt) of a high molecular weight high density polyethylene (HMW-HDPE) resin and a high molecular weight low density polyethylene (HMW-LDPE) resin. Also disclosed is the direct reactor formation of this polymer. The new polymer can be used to manufacture high gloss, low haze films and to form easy to open bags. The present invention is also directed to a method of improving the haze properties of clear plastic films prepared from high molecular weight high density polyethylene (HMW-HDPE) resins, which method comprises adding a haze reducing amount of a high molecular weight low density polyethylene (HMW-LDPE) resin to said HMW-HDPE resins and forming films from the blended and extruded resin mixture.

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# POLYMERIC MATERIAL AND CLEAR FILM PRODUCED THEREFROM

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# CROSS-REFERENCE TO RELATED APPLICATIONS

In the United States Patent and Trademark Office, this application is a continuation-in-part of copending application Serial No. 07/677,534, filed 29 March 1991, the disclosure of which is hereby incorporated herein by reference.

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# BACKGROUND OF THE INVENTION

The present invention is directed to improvements in high density, and particularly, high density, high molecular weight polyethylene polymers, the use of such improved polymers in film and bag applications, and to a method of producing such improved polymers.

High density polyethylene (HDPE) polymers have traditionally not been employed in the production of thin plastic films, plastic bags, and the like, which require high clarity, because these materials do not possess the requisite degree of clarity most commonly desired for many thin plastic film uses. Thus, when clear (or semi-clear) plastic (i.e., polymeric) films

or bags are formed, they are usually formed from low density polyethylene (LDPE) or mixtures of low density polyethylene polymers. Conventional HDPE films and/or bags, unlike LDPE films and/or bags have little or no gloss in their overall appearance, often making them undesirable to wholesale and retail consumers alike. In the United States, the following companies produce the bulk of HDPE; Phillips 66, Exxon/Paxon, Occidental Chemical, Quantum Chemical, Solvay Polymers, Chevron Chemical, Union Carbide, Dow Chemical, and Hoechst Celanese. See, Chemical & Engineering News, Vol. 70, No. 12, pp. 9-10, March 23, 1992.

Thin, clear plastic films and thin clear plastic bags, such as plastic produce bags, have traditionally 15 been prepared from low density polyethylene (LDPE) These materials are generally used because they can be cheaply formed into films, and the bags produced therefrom can also be made easily and at relatively low cost. However, the LDPE materials are not without 20 their drawbacks. LDPE films and bags produced therefrom are typically very clingy, thus making the bags hard to open. LDPE films and bags produced therefrom are not as strong as HDPE films and bags at an equivalent thickness. In addition, LDPE films are 25 more flexible than HDPE films, which can make LDPE more difficult to run through machinery. The higher stiffness of HDPE films is one very desirable characteristic of this type of product, but the lack of high gloss and clarity has limited its applications.

The present invention represents a dramatic breakthrough in the use of high density polyethylene polymers for the formation of clear, strong thin films

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and bags. The present invention affords a high density polyethylene material which can be formed into a thin film having many of the desirable qualities of both high and low density polyethylene materials, without the disadvantages associated with either class of material.

Being a high density product, the film and/or bags produced therefrom are stronger at an equivalent thickness, have the requisite high clarity, and have 10 less cling than those films and/or bags formed from traditional low density polyethylene polymers. Since the polymer of the present invention is a high density polyethylene, less polymer is required to form a film or bag having superior strength characteristics in 15 comparison to the traditional low density polymers. addition, since the polymer of the present invention is a high molecular weight, high density material, it yields a stiffer film and/or bag at comparable thicknesses to a conventional LDPE polymer, which makes 20 the processing of the film through machinery better, and extends the applications of the material beyond that traditionally envisioned for LDPE films and/or bags.

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### INFORMATION DISCLOSURE

Applicants wish to cite the following patents as representative prior art with respect to the invention claimed herein.

U.S. Patent No. 2,983,704 (Roedel) describes a film of polyethylene comprising a solid ethylene polymer having a density of 0.9137 at  $25^{\circ}$ C, and from 10 to

50% by weight of an ethylene polymer having a density of 0.9757 at  $25^{\circ}$ C.

- U.S. Patent No. 1,234,567 (Tritsch) describes a pressure-sensitive adhesive tape having a molecularly oriented polyethylene film backing and a pressure-sensitive adhesive mass on at least one side thereof, said backing comprising a blend of high density polyethylene having a density of from about 0.95 to about 0.98 and low density polyethylene having a density of about 0.92 wherein said high density polyethylene is present in an amount from about 5% to less than about 20 percent of the blend.
- U.S. Patent No. 3,125,548 (Anderson) describes a polyethylene blend comprising 20 to 45 weight percent of a polyethylene having a density of less than 0.920 g/cc, 30 to 60 weight percent of a polyethylene resin having a density of 0.1924 to 0.933 g/cc and at least 10 weight percent of a polyethylene resin having a density above 0.945 g/cc.
  - U.S. Patent No. 3,176,051 (Gregorian et al.) describes a blended composition, comprising polyethylene having a density in the range 0.94 to 0.97 and a melt index in the range 0.5 to 10 and a minor amount, i.e., between 0.1 to 10% by weight of said composition of an additive member of the group consisting of polyethylene having a reduced viscosity in the range 2.9 to 10 and a copolymer of ethylene and 1-butene having a reduced viscosity in the range 4.0 to 10.
    - U.S. Patent No. 3,340,328 (Brindell et al.)

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describes a homogeneous, polyethylene composition comprising a blend of (a) from 15 percent to 25 percent by weight of a straight chain polyethylene characterized as having a density of from 0.95 g/cc, to 0.96 g/cc, at 23°C, and in having a melt index in the range of 3 to 15 g/10 minutes through a 2.1 mm orifice at 190°C, and under a 2.16 kg weight; and (b) from 85 percent to 75 percent of a linear polyethylene having an average molecular weight exceeding 750,000 and characterized as having a density of between approximately 0.925 g/cc, and 0.935 g/cc, at 23°C, a melt index of about 0.3°0 g/10 minutes at 250°C, and 2,740 p.s.i., and an initial melting point of between 186°C, and 220°C.

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U.S. Patent No. 3,231,636 (Snyder) describes a composition possessing improved shear strength and resistance to thermal embrittlement comprising 50 to 85 parts by weight of a polyethylene resin having a specific gravity above 0.945 and a melt index between about 0.02 and 8.0 and 50 to 15 parts by weight of a polyethylene resin having a specific gravity between about 0.915 and 0.925 and a melt index between about 0.02 to 25.0.

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U.S. Patent No. 3,375,303 (Joyce) describes a composition comprising low density polyethylene having a density of from about 0.915 to about 0.925 and from about 1 to about 9 percent by weight, based on the weight of the composition of high density, high molecular weight polyethylene of narrow molecular weight distribution having a density of from about 0.930 to about 0.965, a melt index of not more than 0.1 decigrams per minute measured at 44 p.s.i. and 190°C,

3.0

and a melt flow of not more than 10 decigrams per minute measured at 440 p.s.i. and 190°C, the melt index of said low density polyethylene being no greater than about 30 times the melt index of the high density polyethylene.

U.S. Patent No. 3,381,060 (Peacock) describes a composition exhibiting freedom from melt fracture comprising low density polyethylene having a density of from about 0.915 to about 0.925, from about 0.3 to 10 about 8 percent by weight of a first high density polyethylene having a density of from about 0.930 to about 0.965, a melt index of not more than 0.1 decigram per minute measured at 44 p.s.i. and 190°C, and a melt flow of not more than 10 decigrams per minute measured at 440 p.s.i. and 190°C, and from about 1 to about 33 percent by weight of a second high density polyethylene having a density of from about 0.930 to about 0.965, a melt index of greater than 0.1 decigram 20 per minute measured at 44 p.s.i. and 190°C, and a melt flow of greater than 10 decigrams per minute measured at 440 p.s.i. and 190°C, the melt index of said low density polyethylene being no greater than about 250 times the melt index of said first high 25 density polyethylene.

The following literature references deal with the potential correlations of polyethylene film rheological properties with other physical properties, especially film optical properties.

S. Onogi, et al., <u>Polymer Journal</u>, 7 (4), 467-480 (1975) entitled "Rheo-Optical Studies of Drawn Polyethylene Films." This reference describes how

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birefringence and stress relaxation were measured simultaneously on low density polyethylene (LDPE) films drawn to various extents. For undrawn and weakly drawn films, the strain-optical coefficient increased with increasing time; for highly drawn films, it decreased with increasing time; indicating that highly drawn films do not exhibit the mechanism of crystalline orientation. No melt rheology was performed.

- M. Shida, et al., <u>Polymer Engineering and Science</u>, 17 (11), 769-774 (1977), entitled "Correlation of Low Density Rheological Measurements with Optical an Processing Properties." This paper describes physical properties such as film haze and gloss of low density polyethylene (LDPE), which were correlated with rheological functions and the level of long-chain branching.
- M. Rokudai, et al., <u>Journal of Applied Polymer</u>

  Science, 23, 3289-3294 (1979), entitled, "Influence of Shearing History on the Rheological Properties and Processability of Branched Polymers. II. Optical Properties of Low-Density Polyethylene Blown Films."

  In this paper, the authors discuss the rheological and optical properties of six (6) different LDPE resins, which were determined on both fresh samples and samples that had been extruded five (5) times to determine the effects of extrusion shearing. The modifications effected by shearing were correlated with a rheological property called the "processing index" (PI).
  - F.C. Stehling, et al., <u>Macromolecules</u>, 14, 698-708 (1981), entitled "Causes of Haze of Low-Density Polyethylene Blown Films." In this paper, static and

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on-line haze, low-angle light scattering, and microscopic measurements showed that haze of LDPE films is caused mainly by scattering from rough film surfaces that are formed by two mechanisms:

- melt flow disturbances at the die exit
   (extrusion haze)
  - stress-induced crystallization close to the film surface (crystallization haze).

Haze from melt flow disturbances can be reduced by selecting resins that contain relatively low concentrations of large molecules and by intense mechanical deformation of the melt before extrusion.

Melt index swell decreased with number of extrusions and correlated well with degree of haze reduction.

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- H. H. Winter, <u>Pure Appl. Chem.</u>, 55 (6), 943-976 (1983), entitled, "A Collaborative Study on the Relation Between Film Blowing Performance and Rheological Properties of Two Low-Density and Two High-Density Polyethylene Samples." In this paper two pairs of polyethylenes (HDPE an LDPE) were studied in 14 laboratories. The experiments concentrated on film blowing and laboratory tests. The resins were chosen so that their shear flow behavior was similar, but their film blowing properties differed. Laboratory tests included the following:
  - 1. Crystallization from the melt
  - Shear viscosity (steady and time dependent)
  - 3. Storage and loss moduli
  - 4. Relaxation modulus
  - 5. Entrance pressure correction
  - 6. Melt flow index
  - 7. Extrudate swell

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Uniaxial extensional creep and recovery afterward

9. Tensile test on extrudate

The author claimed that extensional flow tests were the most sensitive, but other sensitive rheological tests included those that were dominated by long time constants. This includes the complex modulus.

- S.A. Montes, Polymer Engineering and Science, 24 (4), 259-263 (1984), entitled "Rheological Properties 10 of Blown Film Low-Density Polyethylene Resins." In this paper the author found that viscoelasticity played a dominant role in the behavior of three blown film-grade low density polyethylene resins. He mentioned, for instance, that there was general 15 agreement that haze in LDPE film increases as extrudate swell, a measure of elasticity, increases. He also mentioned that rough films are generated by two mechanisms: extrusion haze and crystallization haze. 20 Extrusion haze involves melt flow disturbances at the die exit and is, therefore, related to the rheological properties of the resin.
- H. Ashizawa, et al., <u>Polymer Engineering and</u>

  Science, 24, (13), 305-1042 (1984), entitled, "An Investigation of Optical Clarity and Crystalline Orientation in Polyethylene Tubular Film." In this paper the authors claim that the majority of light scattered from LDPE, LLDPE and HDPE film was from the surface and not from the interior.
  - M.S. Pucci et al., <u>Polymer Engineering and Science</u>, 26 (8), 569-575 (1986), entitled "Correlation of Blown Film Optical Properties with Resin Properties. In this

paper it was shown that for LDPE blown films, resins with higher melt elasticity consistently resulted in films with poorer optical properties.

- J. Audureau, et al., <u>Journal of Plastic Film & Sheeting</u>, 2, 298-309 (1986), entitled "Prediction and Improvement of Surface Properties of Tubular Low Density Polyethylene Films." In this paper, the authors found a correlation between surface haze and the ratio of freeze time to average rheological relaxation time. The average rheological relaxation time was obtained from dynamic melt rheological data.
- W. Minoshima et al., <u>Journal of Non-Newtonian Fluid</u>

  Mechanics, 19, 275-302 (1986), entitled, "Instability
  Phenomena in Tubular Film, an Melt Spinning of
  Rheologically Characterized High Density, Low Density
  and Linear Low Density Polyethylenes."
- D.L. Cooke et al., Journal of Plastic Film & 20 Sheeting, 5, 290-307 (1989), entitled "Addition of Branched Molecules and High Molecular Weight Molecules to Improve Optical Properties of LLDPE Film." In this paper the authors mention that haze and gloss of LLDPE films are determined largely by the roughness of the 25 film surface. The LLDPE crystallization process that is responsible for the roughness can be disrupted by blending a small amount of a second PE resin. The resins used for blending with LLDPE included high gloss-low haze LDPE, low gloss-high haze LDPE, and HDPE. The authors suggest that a blending resin that has a high molecular weight tail in its MWD is most effective in improving LLDPE optical properties.

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Rheometrics Application Bulletin, No. 11 (undated), entitled, "Melt Elasticity & PE Blown-Film Optics." In this bulletin prepared by a commercial manufacturer of rheology instrumentation, the author reports correlations between the haze in low density polyethylene films and the storage modulus, G'. The differences in the G' values were greatest in the low frequency region, 0.1 to 1 rad/sec.

10 From the art discussed above, there is certainly an interest in the production of clear plastic films, such as those described and claimed herein.

### SUMMARY OF THE INVENTION

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The present invention is directed to a high molecular weight, high density polyethylene (HMW-HDPE) polymer which can be formed into a thin film having many of the desirable qualities of both high and low density polyethylene materials, without the disadvantages commonly associated with either class of material.

- The HMW-HDPE polymer of the present invention has a molecular weight range of about 450,000 to 650,000, a density range of from about 0.941 to 0.950, and a melt index of about 0.5 g/10 min.
- Thin films produced from this composition have the following physical properties:
  - (a) Low haze (i.e., high clarity); the percentage of haze in the films of the present

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invention is less than about 50 percent, preferably less than about 35 percent, and most preferably less than about 20 percent, as measured by ASTM D-1003. Conventional HDPE polymer based films have haze values typically in excess of 50, 60 and/or 70 percent when measured in this manner. (See Table I and II, infra).

(b) High Gloss (45°); the 45° gloss values of the films of the present invention are at least about 20, preferably at least about 30 and most preferably at least about 40, as measured by ASTM D-2457. Conventional HDPE polymer based films have gloss values typically below about 15 and/or 10 when measured in this manner. (See Table I and II, infra).

of light transmission; the percentage of light transmission for the films of the present invention are at least about 85 percent, preferably at least about 90 percent, as measured by ASTM D-1003. Conventional HDPE polymer based films have similar high light transmission percentages. Thus, the HDPE polymer of the present invention retains this favorable characteristic. (See Table I and II, infra).

(d) Variation of Moisture Vapor

Transmission; the films of the present
invention show variation in moisture vapor
transmission (MVTR) values when compared to

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conventional HMW-HDPE polymer films as measured using ASTM F-372. In some cases the MVTR values increased from about 3 to 20 percent; while in other cases MVTR values decreased up to about 10 percent. (See Table I and II, infra).

- (e) Increased Nitrogen Gas Permeation; the films of the present invention show an increase in N<sub>2</sub> gas permeation values when compared to conventional HMW-HDPE polymer films ranging from about 1.5% up to about 17.2% as measured using ASTM D-3985. (See Table I and II, <u>infra</u>).
- (f) Increased Oxygen Gas Permeation; the films of the present invention show an increase in O<sub>2</sub> gas permeation values when compared to conventional HMW-HDPE polymer films ranging from about 3% up to about 22% as measured using ASTM D-3985. (see Table I and II, <u>infra</u>).
- (g) Low Coefficient of Friction; the films of the present invention have a low coefficient of friction as measured using ASTM D-1894.

As used herein, the term "thin films" is defined 30 as a film having a thickness of less than 1.5 Mil, preferably less than 1.0 Mil, and most preferably less than 0.75 Mil.

In one preferred embodiment, it has been discovered

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that by blending and extruding a mixture comprising a high molecular weight, high density polyethylene (abbreviated HMW-HDPE) resin (e.g., Novacor Chemical's Novapol, Product Number HD-4045, also know as HF-W648-H) and a high molecular weight low density polyethylene (abbreviated HMW-LDPE) resin (e.g., Quantum USI's Petrothene, Product Number NA 355) a novel polymeric material is produced.

While not wishing to be bound by theory, it is 10 believed that the resulting polymer formed by the above described blending and extrusion is not merely a mixture of the individual ingredients. It is believed that during the extrusion process, the crystalline structure of the two individual polymers is modified. resulting in the formation of a new polymer. Such change is believed due to the action of the heat and pressure of the extruder. This new polymer affords films and/or bags exhibiting high strength, high clarity, high gloss, low haze, and high slip. The film and/or bags prepared from this new polymer have exceptional strength, high gloss or sheen, and better transparency than conventional HMW-HDPE film based bags.

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It has further been discovered that the addition of a HMW-LDPE resin to any HMW-HDPE resin significantly reduces the haze value of the combination polymer, while concomitantly raising the gloss value of a film produced therefrom. Thus this invention is also directed to a method of improving the haze properties of clear films prepared from high molecular weight high density polyethylene resins, which method comprises adding a haze reducing amount of a high molecular

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weight low density polyethylene resin to said HMW-HDPE resins and forming films from the blended resin mixture.

The above described improved physical properties of films and bags prepared from a blend of HMW-HDPE resins and HMW-LDPE resins are essential for the commercial and customer acceptance of thin film materials, particularly thin film clear bags, such as produce and bakery bags, dry cleaning bags, and the like.

Through experimentation it has been determined that one of the most preferred formulations of the aforementioned blend of a HMW-HDPE resin and a LDPE resin in this invention is 80% (by weight) of Novacor's Novapol HD-4045 and 20% (by weight) of Quantum USI's Petrothene NA 355. The ranges of these materials which can be effectively used to make the film and/or bags of the present invention are as follows:

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Novapol HDPE No. HD-4045 90% - 10% (by weight)

Quantum LDPE No. NA 355 10% - 90% (by weight)

A second preferred polymer blend formulation which has been developed herein is 79% Novacor's Novapol HD-4045, 20% USI's Petrothene NA 355 and 1% Archer Daniels Midland's Polyclean II 20835. It should be noted that USI's Petrothene NA351 can be substituted for the NA 355. Also, USI's Petrothene NA357 is another acceptable material.

# DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As described above, the present invention is directed to improvements in high density polyethylene (HDPE) polymers, the use of such improved polymers in film and bag applications, and to a method of producing such improved polymers.

More particularly, the present invention is directed to a novel polymeric material and most particularly to films and/or thin, strong, high clarity bags, (e.g., produce and bakery bags) produced from this polymeric material.

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The physical properties for various HMWW-HDPE 15 polymers and blended compositions useful herein are presented below in Tables I and II. These data are for films produced at a 4:1 blow-up ratio, which is adequate for purposes of the present invention. currently preferred blow-up ratio for film production 20 in this invention is 5:1, and at that ratio, most of the properties described in the data Tables are improved. With the exception of Example F-1 in Table I, the mixed film compositions recited were produced by a physical blending (mixing) of the solid polymers, 25 followed by extrusion. In the case of Example F-1, the polymers were compounded together (melted together) prior to extrusion. From these data and the general level of skill in this field of art, the skilled artisan will be capable of determining, without resort to undue experimentation, other suitable materials which will yield a film and/or bag having the properties described herein.

TABLE I

# Physical Properties for various HMWW-HDPE and FRESH-SAC Formulations

		A 100%	В	.C	D 80%	Ε	F 80%
		USI	100%	100%	Mitsui	100%	Novacor
		LY-	Chev	Cain	20%	Mitsui	20%
		600	9690	L5005	NA-335	7000F	NA-355
		000	5050		1177_000	7000	<u> </u>
Dart Impact G/Mil		281	251	254	48	1214	25.7
·							
Puncture J/mm		43.8	42.4	62.5	46.8	83	48.5
			1				
Elmendorf Tear G/Mil							
	MD	8.8	19.0	11.6	7.8	8.9	9.3
	TD	206	93	203	425	169	351
			i .	1	1		
MVTR/100sq in/24 hrs		1.59	11.67	1.44	1.68	1.44	2.10
Gas Permeation N2=cc		239	239	188	212	207	268
N2/100 in2/24 hrs				1			
			1				
Gas Permeation O2=cc		803	874	809	871	693	997
O2/100 in2/24 hrs							
Gloss (45o)		6.4	10.0	7.1	36.9	11.1	40.7
					1		
Haze (%)		72.1	59.9	70.5	17.7	58.7	19.2
Light Transmission (%)	•	91.5	92.0	91.6	92.8	92.1	92.8
			1				
Tensile Yield PSI							
	MD	4814	5162	4074	6090	5582	13871
	TD	3625	3828	3741	3219	3987	3306
Tensile Strength							
	MD	11165	9625	8511	12905	10295	19570
	TD	6104	6148	5655	4422	16133	4886
Elongation			1	ļ	<u> </u>		
	MD		263	324	232	242	1306
	TD	571	539	538	601	587	605
							<u> </u>
Secant Modulus							
	MD	133545	130790	112955	151380	159935	95555
	TD	139345	147345	134415	153265	188210	127890
					1	1	
Thickness (Mil)		.55	.61	1.63	1.57	1.58	1.67

TABLE 1

Physical	Proper	ties	for va	rious			• •	
LIXANATAL.	HUDE	and	FRES	HLSA	C	Form	ulatio	ns

	 5		•				
		F-1	G	Н		j	K
		Compounded		80%	80%	70%	80%
		80% Novacor		LY600	Chev	Mitsui	Mitsui
	•	20% Quantum	20%	20%	20%	30%	20%
		USI NA355	NA355	NA355	NA355	NA355.	Rep.
					**	<u> </u>	<del></del> ,
Dart Impact G/Mil	: [	65	39.2	38.3	32	116	1400
Puncture J/mm		57	58.2	47.6	43.7	49.4	77.2
						<u> </u>	
Elmendorf Tear G/Mil	٠	<del> </del>					
	MD	6.4	8.6	7.5	7.4	7.6	18.4
	TD	143	385	396	351	380	230
							·
MVTR/100sq in/24 hrs		***	1.49	1.44	1.51	1.49	1.46
WW 1711 1003Q 11112-4 1113		7 7 7		<u> </u>			
Gas Permeation N2=cc		*** :	227	243	1241	215	210
N2/100 in2/24 hrs				1			1
N2/100 In2/24 IIIS	. :			<del> </del>	-	<del>                                     </del>	
0 - 0 - 0 - 0		***	703	939	901	886	705
Gas Permeation O2=cc	•		1700	1000	1	1	
02/100 in2/24 hrs		<b> </b>	<del> </del>	-	<del> </del>	<del>                                     </del>	<del>†                                      </del>
			107.0	OF 6	39.1	39.9	13.2
Gloss (450)		55.0	27.8	25.6	39.1	33.3	10.2
				<del> </del>	100	100	161.2
Haze (%)		7.9	27.2	30.5	18.1	16.3	101.2
			<u> </u>		1		101.0
Light Transmission (%)		93.0	92.7	92.4	91.9	93.1	191.9
				<u> </u>			1
Tensile Yield PSI			1.			<u> </u>	· ·
	MD	4626	5582	4611	3764	6131	5462
	TD	3045	3461	3582	3314	3320	4120
Tensile Strength							
	MD	10585	11078	10251	9438	11841	19895
	TD	4495	4988	4988	4899	4462	6241
			1	1			
Elongation			<del> </del>				
Eiongauon	MD	172	200	286	298	229	252
	TD	578	559	541	583	648	601
	٠,	378	1000	<del> </del>	+	1	<del>                                     </del>
		-	+		+	+	+
Secant Modulus			1445-05	140000	02000	153380	160921
	MD		111795	148896	93286		
	TD	113680	141230	134621	125290	155271	188231
	٠.						1
Thickness (Mil)		.54	.59	.60	.59	.58	1.60

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# TABLE I

# Physical Properties for various HMWW-HDPE and FRESH-SAC Formulations

		L	M 100%	N 80%	0	P 80%
		100%	American	American	100%	Formosa
		Novacor	Hoechst	Hoechst	Formosa	905(F)
		HFW945-H	GM9255	20% NA355	905(F)	20% NA355
Dart Impact G/Mil	[	400	481	74.1	234	67
	Ì					
Puncture J/mm	Ì	72	77.0	61.0	70.0	45.0
, 5.15151-5-511	Ì	<del> </del>				
Elmendorf Tear G/Mil	Ì		İ			
Eliticitadi i real Grissi	MD	15	0.61	4.8	9.0	7.9
		143	134	249	226.0	231.0
		140	1		<u> </u>	
MATERIA 0000 in/04 hrs		1.66	1			***
MVTR/100sq in/24 hrs		1.00		<u>.                                      </u>	<u>.                                    </u>	
		-	1 ***	***		1
Gas Permeation N2=cc		240	ļ	<del> </del>	1	
N2/100 in2/24 hrs				ļ	<del> </del>	
				1000	1	• • •
Gas Permeation O2=cc		869				
O2/100 in2/24 hrs				<u> </u>	ļ	
•					<u> </u>	<u> </u>
Gloss (450)		11.2	8.0	34.3	8.5	31.0
				1		
Haze (%)		54.3	63.7	17.8	62.0	22.9
Light Transmission (%)	•	91.9	91.7	192.7	92.0	93.0
		ļ				
Tensile Yield PSI				1		i
Tensile Tiele . C.	MD	5150	5350	4540	4437	3944
		392B	4350	14600	3524	2958
	10	3320	17000	-		
Tanalla Bananah			<del> </del>	<u> </u>		1
Tensile Strength		0200	0410	19730	89176	9034
		9300	9410	15307	5031	4466
	10	7000	7177	5307	15031	14400
					<del>-</del>	
Elongation		<u></u>	<del></del>	1000	1012	1000
	MD	300	241	222	313	282
	TD	500	555	545	589	591
					<del></del>	<del>                                     </del>
Secant Modulus						
	MD	103000	152830	117740	113245	109620
	TD	115000	1166895	1166460	126730	132240
	_					
Thickness (Mil)		.50	.55	1.60	.62	1.62
THEKHESS (MIII)						

<u>: 20 -</u>

#### TABLE I

Physical Properties for various HMWW-HDPE and FRESH-SAC Formulations

		Q	R ,	
			80%	
		100%	Formosa 908(	F)
		Formosa	20% Quantum	1
		908(F)	USI NA355	
Dart Impact G/Mil		207		
Dart Impact Crimi				
Puncture J/mm		58.0	50.0	
Pulicture Ovinin	٠.,	30.0		
Firm CAR		<u> </u>		
Elmendorf Tear G/Mil		<u> </u>	7.3	٠
	MD	9.5		
	TD'	173.0	324.0	
	· .;	•••	1000	
MVTR/100sq in/24 hrs				
				٠.
Gas Permeation N2=cc		***	***	
N2/100 in2/24 hrs				
			1	
Gas Permeation O2=cc		• • •	1***	
O2/100 in2/24 hrs	. '			
Gloss (450)		7.7	30.0	٠.
Haze (%)		70.0	21.9	
Light Transmission (%)	·	92.0	93.0	
Light (valienticolor) (va)	• •	-		
Tensile Yield PSI				٠.,
rename ricio i ei	MD	4205	3364	
	TD	3350	3219	
		0000		
Topollo Strongth			<del></del>	٠.
Tensile Strength	MD	7105	7206	•
	TD	4930	4016	
	٠ ، ب	4530	140.0	
·				
Elongation		000	1001	
	MD	<del></del>	231	1
	TD	581	633	
Secant Modulus			1-0-0	
	MD	`	79750	
	TD	133545	128905	
	2 É.			
Thickness (Mil)		.49	.56	

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# FOOTNOTE TO TABLE I

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	A= B=	100% Quantum USI LY6000 100% Chevron 9690
	C-	100% Cain L5005
	D-	80% Mitsui 7000F
10		20% Quantum USI NA355
	E•	100% Mitsui 7000F
	F•	80% Novacor HFW-945-H
		20% Quantum USI NA355
	F-1•	Compounded 80% Novacor
		20% Quantum USI NA355
	G-	80% Cain L-5005
15		20% Quantum USI NA355
	H=	80% Quantum USI LY6000
		20% Quantum USI NA355
	j=	80% Chevron 9690
		20% Quantum USI NA355
	J=	70% Mitsui 7000F
		30% Quantum USI NA355
20	K•	80% Mitsui 7000F
		20% Repro. Novacor HFW-945-H
	<u>L</u> =	100% Novacor HFW-945-H
	M=	100% American Hoechst GM9255
	N=	80% American Hoechst GM 9255
		20% Quantum USI NA355
	0-	100% Formosa 905(F)
25	P•	80% Formosa 905(F)
		20% Quantum USI NA355
	Q=	100% Formosa 908(F)
	R=	80% Formosa 908(F)
		20% Quantum USI NA355

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Table II provides additional physical data for some of the polymeric formulations described in Table I.

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TABLE 11

SAMPLE	٧	B	၁	Ω	Ħ	ı	S	H	1	· ·	Ж	L	Σ	z
TEST - UNITS														
														İ
D.S.C. C	133.7	131.1	130.9	130.2	131.7	128.9	128.5	131.0	129.6	130.0	130.6	129.7	132.0	129.4
	.255	.240	.220	.220	.205	.215	.235	.230	275	.235	.225	.240	.270	.307
Gloss (45°)	19.0	10.0	7.00	38.0	11.0	39.0	27.0	25.0	33.0	36.0	13.0	15.0	8.3	32.0
Haze %	71.3	59.3	68.30	17.8	57.7	18.9	27.6	30.0	22.2	20.7	57.5	48.9	63.1	18.4
Density g/cm <sup>3</sup>	.9521	.9485	.9497	.9468	.9530	.9411	.9410	.9460	.9424	.9455	.9532	.9463	.9517	.9459
MW - DISTRIBUTION														
NO Average	30.3	37.9	27.5	18.1	25.5	34.0	23.1	30.5	42.3	27.6	26.5	34.3	28.4	28.8
WT - Average	630	721	899	326	678	560	394	421	629	589	675	617	261	432
Z - Average	2965	3810	3269	2074	3426	3540	2446	2315	4225	3214	3508	3600	2615	2072
VIS - AVERAGE														
Dispersity	20.9	19.1	24.3	18.0	9:92	16.3	19.1	13.8	15.6	21.5	25.5	18.1	19.8	15.1
														ı

\* - see footnote to TABLE I for formulation key (samples A-N).

As shown in Tables I and II, either compounding (i.e., co-melting and mixing) or blending (i.e., solid mixing) of the various polymeric starting materials may be conducted prior to extrusion, and following extrusion the new polymeric material is obtained. In one case, the new polymer may be formed during the compounding, in the other, it is clearly formed in situ (i.e., in the extruder).

While one route used to prepare the novel polymeric 10 composition of the present invention is based upon the physical blending of two (or more) materials together, followed by extrusion of the blend to produce the novel polymeric product, it is envisioned other processes may be employed. For example, given the physical 15 properties of the presently claimed polymeric composition, those artisans having ordinary skill in the polymer art will be able to prepare the same polymeric product, having the described desired properties, using a variety of different techniques, e.g., in a polymer reactor vessel. In other words, the present inventors anticipate that artisans having ordinary skill in this field will be able to avoid the blending step described above, and still produce the presently claimed polymeric composition. Such progress 25 is a typical development in the production of polymers, and is one that is clearly envisioned by the present inventors to represent the ultimate best mode for producing the presently claimed polymer composition. In fact, Exxon and Dow Chemical have recently published 30. technical literature wherein the describe new catalysts that permit them to tailor specific resins having specific properties in polymer reactor vessels.

Thus, any high molecular weight polyethylene based polymer exhibiting the previously described properties, prepared by whatever means, is deemed to be encompassed by the present application and the present claims.

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As discussed above, clear produce and bakery bags manufactured from conventional HDPE resins could be produced using up to 50% less polymer resin than used for conventional LDPE produce and bakery plastic bags, but the HDPE resins have not generally been used in such thin bag applications because previously existing HDPE products were unable to match the clarity of the LDPE product. There is a general consensus that grocery store customers and check-out personnel need to see the contents of the bag without resort to opening the same, particularly in today's fast paced checkout lanes. The bags and film of the present invention provide the level of clarity necessary for this market, preferably in an easy-to-open T-shirt type bag form.

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The novel polymer of the present invention has exceptional properties, which allows its use in numerous film and/or bag applications, including:

25 (a) as a substrate for adhesive laminating, e.g., for pouch packages where high clarity, high strength at reduced gauge, high modulus and

heat stability are important.

30 (b) as a "can-liner" for garbage or recycling cans or bins, which represents the first high clarity, HMW HDPE product of its type; particularly for municipal recycling programs.

PCT/US92/02557 WO 92/17539

- as a carton liner, where high clarity, high (c) barrier (gas) properties are important, e.g., in baking dough transfer and the like.
- (d) a variety of clear, strong bag constructions, including for example, side weld, bottom gussett, tubular, and the like, for use as lettuce bags, various food packs, e.g., deli pouches, garment bags, e.g., dry cleaning bags, and the like. 10

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- as a clear and strong film wrapper, e.g., for (e) newspapers, automatic packaging machines, and the like.
- as a heat sealable (hermetically sealable) (f) single-ply replacement for polyester and/or polypropylene film/bag applications.
- as a substrate film for metallization and high (g) 2.0 moisture, light and air barrier food bags prepared therefrom (e.g., coffee, snack foods, such as candy, chips, peanuts, etc.) traditionally formed from polyester and/or two-layer polypropylene products.
  - as a heat stable film material, e.g., to be (h) used to cover food for microwave warming, heating and cooking.
  - (i) as a solarization film for agricultural uses; e.g., as a crop or ground cover wherein radiant heat energy from the sun is captured and directed to plants and/or the soil,

promoting physical, chemical and/or biological changes therein.

Upon consideration of this disclosure, the skilled artisan in this field will readily be capable of determining additional uses for the polymer, film and bags of the present invention.

For instance, the mixture of HMW-HDPE (e.g.,

Novapol's HD-4045) and the HMW-LDPE (e.g., Quantum's NA

355) can be run through a commercial blown film

extruder to produce films ranging in thickness from

about 0.000275 inches to about 0.0005 inches.

Quantum's NA 355, one of the preferred resins used herein includes the following guidelines for its use:

A long-stalk bubble shape is recommended if
HMW-LDPE films under 1.5 mil are being extruded. In
this technique, the extrudate above the die is kept at
the same diameter as the die until the bubble expands
to its final diameter just below the frost line, the
point where the molten resin solidifies. The long
stalk is maintained by a single-lip air ring around the
die.

The rapid expansion of the bubble immediately below the frost line creates an orientation in the melt which optimizes the resultant film's impact strength. This further enhances HMW-LDPE's strength properties, particularly at thin gauges.

Drawdown is also increased when long-stalk extrusion is used. Field trails have shown that

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PCT/US92/02557

Quantum's HMW-LDPE resins can be drawn down to 0.5 mil and retain their high strength and clarity properties, provided they are extruded using the long-stalk technique. Table III lists other properties of Quantum's HMW-LDPE resins for film when blown under long-stalk conditions.

TABLE III

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Property	Units	ASTM Test Method	NA 351-226	NA 355-196	NA 357-103
Resin	c/10 min	D 1238	0.3	0.5	0.25
Melt Index	g/10 min.				
Density	g/cm <sup>3</sup>	D 1505	0.925	0.925	0.930
Vinyl Acetate incorporated	%		<del>-</del>	-	4.5
Film Haze	%	D 1003	6.0	5.8	8.0
Gioss, 45°		D 2457	67	69	60
	g	D 1709	310	300	350
TEDD, Body	ft-lb ft-lb	D 4272 D 4272	2.1 2.0	2.0 1.9	3.8 3.8
Instron Puncture		:			
Force	newtons		27	24	24
Energy	J		0.44	0.42	0.42
Tensile Properties					
Break, MD	psi	D 882	5300	5400	5200
TD	psi	D 882	5100	5200	5800
Yield, MD	psi	D 882	1900	1840	2200
TD	psi	D 882	1900	1860	1500
Elongation, MD	%	D 882	210	200	310
TD	%	D 882	340	340	310
1% Secant	٠.		٠.		
Modulus, MD	psi	D 882	37,500	32,400	22,800
TD	psi	D 882	42,100	36,400	26,600

All film properties obtained on 1 mil film extruded with a long stalk and 3:1 blow-up ratio.

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Novapol HD-4045 is a high molecular weight, high density film resin for thin gauge, high-strength film applications. This material is advertized by its manufacturer as being designed to be drawn as low as 13 microns (0.5 mil). HD-4045-H offers the film processor high output rates for demanding film applications such as merchandise bags, T-shirt bags, can liners, mailing envelopes and other paper replacement end-uses.

10 HD-4045-H is said to process well on blown film lines designed for high density polyethylene extrusion, as well as on low shear, low L/D grooved barrel extruders. Film produced from this resin can readily be treated, printed and heat sealed on a variety of converting equipment.

Table IV outlines physical properties of HD-4045-H of importance in the present invention.

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## TABLE IV

	, .				
5.	ASTM TEST METHODS	<del>•</del>		<b>⋖</b>	
	AST TEST ME	D 1238 (1) D 1505	_	D 1709/A (4) D 882 D 882	D 882 D 1922
10			13 microns (0.5 mil)		(000 (000
			13 mkron	400 72 (16) 64 (9300) 48 (7000) 300	710 (103,000) 790 (115,000) 15 143
15	ALUES	0 46	(iim 0.1		
	IYPICAL VALUES	10.0	25 microns (1.0 mil)	200 56 (13) 52 (7500) 41 (5900) 450 650	340 (92,000) 340 (107,000) 21 300
20					
	চ	g/10 min g/cm <sup>3</sup>		g/25 mkrons(g/mil) J/mm (in-lb/mil) MPa (psi) WPa (psi) %	(psl) (psl) mkrons (g/m mkrons (g/m
25	UNITS	g/10 g/cm			
		:	(2) (3)	M.D. T.D.	6 M.D. T.D. T.D.
30	PROPERITY RESIN PROPERTIES		FILM PROPERTIES (2) (3)	impact engith	dulus @ 1% Fear
	PROPERTY RESINPRO	Flow Rate Density	FILM PRO	Dart Drop Impact Puncture Tensile Strength Elongation	Secant Modulus @ 1% Elmendorf Tear

<sup>(2)</sup> Film properties are typical of blown film extruded at 4:1 blow-up ratio with a frostline of 6 x die diameter. (3) Data presented are typical but dependent upon operating conditions. (4) Novacor test method.

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While these two materials are especially preferred herein, as shown in Tables I-II, other commercially available high molecular weight high molecular weight high density polyethylenes (HMW-HDPE) can be employed to provide films and/or bags having properties described herein. Such materials include:

Petrothene (R) high density polyethylene resins for blown and cast films (U.S. Industrial Chemicals Co.,) such as LY 600.

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High density polyethylene HD-7000F blown film resin (Exxon Chemical Co.)

Alathon<sup>(R)</sup> L5005 HDPE resin, a high molecular weight HDPE resin (Cain Chemical Inc.) whose broad bimodal molecular weight distribution (MWD) can be controlled by production technology.

Hostalen<sup>(R)</sup> "H" Series HMW HDPE film resins (Hoechst Celanese Co.) have optimal strength in both the machine direction (MD) and transverse direction (TD). Films produced from this resin series are said to possess a naturally slippery surface, allowing for easy opening of thin gauge products.

While a number of HMW HDPE resins have been described, it is similarly believed that the skilled artisan will readily see that NA 355 is not the only HMW-LDPE resin which can be used to improve the gloss and haze values of films and bags prepared from HMW-HDPE resins. Upon consideration of the present disclosure, the skilled artisan will readily be capable

of determining substitute, equivalent, and/or superior materials for formulating polymers, films and/or bags having the unique properties described herein.

- physical analysis of several films prepared according to the present invention (see Tables I-II) has revealed several critical properties, including the following:
- DSC crystallinity measurements of several films prepared according to the present invention reveal that film clarity and haze are not related to the degree of crystallinity of the final film.
- Polymer crystal size is also not related to film clarity and haze, as demonstrated by polarized light microscopy and interference microscopy of microtomed cross sections of film.
- Haze and clarity were found to be related solely to irregular polymer surface features on the inside and outside surfaces of the films. This was initially indicated by interference microscopical examination of film surfaces. This was confirmed by the films becoming optically clear when their surfaces were treated with an immersion oil having a refractive index of 1.5150, similar to polyethylene.
- optical microscopy revealed surface striations on all of the films, even the 100% B film. These straitens, however, are not the cause of haze.

To better characterize the surface irregularities

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on the films, both inside and outside film surfaces were examined using Scanning Electron Microscopy (SEM). Inside and outside surfaces of all films were examined at 100X and 500X. Both film surfaces were also examined at 1000X for A/B blend ratios of 100/0 and 85/15. An analysis of the SEM studies reveal significant differences in surface smoothness and irregularities between inside versus outside surfaces in blend ratios. The degree of surface roughness displayed in these photomicrographs correlates with the loss of clarity for individual films. Film clarity was ranked by measuring how far the film could be lifted off printed material and be legible.

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The present invention will be further illustrated with reference to the following examples which aid in the understanding of the present invention, but which are not to be construed as limitations thereof. All percentages reported herein, unless otherwise specified, are percent by weight. All temperatures are expressed in degrees Celsius.

25 EXAMPLE 1

The Novapol HD-4045 and Petrothene NA 355 are blended together in a 4:1 ratio (i.e., 80% - 20%) respectively. The blend is then run through a blown film extruder at a 4:1 blow-up ratio and produces a 8" X 5" X .0005" X 20,000 foot film roll, [It has been found that a 5:1 blow-up ratio provides better results for most of the physical characteristics.] The film is then printed on by means of a flexographic printing

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press. The film is then converted into a T-shirt sack by a conventional T-shirt bag machine.

### EXAMPLE 2

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Example 1 is repeated, but the formulation comprises 79% Novacor's Novapol HD-4045, 20% USI's Petrothene NA 355 and 1% Archer Daniels Midland's Polyclean II 20835.

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### EXAMPLE 3

Example 1 is repeated, but USI's Petrothene NA 351 is substituted for the NA 355.

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### EXAMPLE 4

Example 1 is repeated, but USI's Petrothene NA 357 is substituted for the NA 355.

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## EXAMPLE 5

Ten films made from various ratios of two polyethylene resins, Novacor's 40/45 (HMW-HDPE) and Petrothene NA 355 (HMW-LDPE), which were designated as Sample A and Sample B, respectively. The blended materials as well as pure pellets of the two components were also submitted for dynamic mechanical testing on the polymer melt, using ASTM D 4440:

30

Instrument:
Temperature:
Environment:
Test Geometry:

Test Frequencies:

Rheometrics System 4 190°C Nitrogen Parallel Plate - 25 mm diameter, with a typic

diameter, with a typical gap height of 1 to 2 mm. 0.1 to 100 rad/sec; 5 points per decade

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Strain Level: 25%

Equilibration time at

test conditions: >5 minutes

for each experiment. Test specimens were loaded at temperatures ranging from 25°C to 70°C. After loading, the temperature was raised in order to melt the specimen. Initially, the specimens underwent thermal expansion and exerted an outward normal force on the parallel plates. Therefore, the gap setting had to be adjusted periodically to avoid a normal force overload to the instrument.

When the temperature reached about 140°C, the

test specimens began to melt, and the normal forces
decreased. The test material was then compressed
between the parallel plates until it clearly filled the
entire gap. Next, the excess material was trimmed from
the edge of the plates. Finally, the test specimen was
compressed again, with the operator making sure that
the entire gap was filled with polymer melt. Once the
temperature of the specimen reached the desired level,
the specimen was allowed to equilibrate for 5 minutes
before testing was begun.

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In preliminary testing, it was determined that a strain level of 25% was suitable for the planned experiments. This selection was based on three criteria:

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 The materials did not exert an excessive torque at the highest test frequency (100 rad/sec).

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2. The materials did exert a sufficient torque at the lowest test frequency (0.1 rad/sec)

3. The materials appeared to be in the linear viscoelastic region, meaning that their rheological properties were not dependent on the strain level.

Multiple runs were performed on each sample until
the degree of reproducibility was acceptable (about 5% difference or less between runs). For some materials, it was sufficient to perform duplicate runs; for others, triplicate runs were necessary.

Tables with data from representative runs for each material are provided below. Since differences between the different samples should be the most noticeable at the low frequencies, this was the region that focused on. The data at the lowest test frequency, 0.1 rad/sec, were somewhat scattered, possibly due to a low torque level or else variations associated with the start-up of the experiment. The scatter at the second-lowest frequency, 0.1585 rad/sec, was acceptably low, so this was the frequency that was used for comparing the different materials.

The results from multiple tests on the unblended materials are given below in Table V. G' refers to the storage modulus; G" refers to the loss modulus.

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TABLE V

5	Material	Form	Expt.	G' (dy/cm <sup>2</sup> ) (*1E-4)	G" (dy/cm <sup>2</sup> ) (*1E-4)
,	A	Pellets	407 408 409 410	7.287 7.500 7.723 7.291	8.337 8.622 8.749 8.510
	A	Film	404 405 406	6.581 6.958 6.928	7.834 8.316 8.378
15			Avg. Std. Cov.(%)	6.822 0.171 3	8.176 0.15 3
20	В	Pellets	412 413 414 Avg. Std. Cov.(%)	1.061 0.987 1.016 1.021 0.030	3.284 3.008 3.080 3.124 0.117
25	В	Film	415 417 Avg. Std. Cov.(%)	1.002 0.998 1.000 0.002	3.060 2.992 3.026 0.034 0

The overall degree of reproducibility was from 2 to 3%. This is considered good.

## SUBSTITUTE SHEET

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Analysis of the storage modulus versus frequency curves of the pellets and films of material A and the pellets and films of material B showed good agreement (data not shown). The corresponding loss modulus values for pellets and films of materials A and B also showed good agreement (data not shown).

3. The Dependence of Rheological Properties on Composition and Correlations with Clarity Data

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The storage and loss moduli for the various compositions at 0.1585 rad/sec are given in Table VI below.

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5		gg	G" (/cm 2) (1E-4)	3.080 8.622	2.992	3.732	4.588	5.635	6.082	5.595	6.828	6.577	8.316
10		of Polyethylene Blends	G' (d/cm 2) (*E-4)	1.016 7.500	0.998	1.752	2.776	3.686	4.124	3.836	5.321	5.156	6.958
15	TABLE VI		Clarity Ranking		ι ч	)	4		3		2		9
	TAI	ss Modu	Expt.	414	417	438	432	430	428	424	423	419	405
20		Storage and Loss Moduli	Form	Pellet Pellet	Film	film	film	Film	Film	Film	Film	Film	Film
25		Storag	Percent B	100	100	70	09	50	40	30	20	15	0
30 ·			Percent A	0 100	0	30	40	50	09	70	80	85	100

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The correlations of both storage and loss modulus with composition are very good. The equations from linear regression are the following:

Storage Modulus = 588 \* (%A) + 4615 r = 0.948

Loss Modulus = 513 \* (%A) + 26477 r = 0.938

However, <u>neither</u> of these quantities correlated with the clarity rankings. Therefore, the unexpected ranking of the clarity of these films cannot be explained by the rheological data, even though correlations between rheological data and clarity have been proposed in several prior art references (supra).

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The present invention has been described in detail, including the preferred embodiments thereof. However, it will be appreciated that those skilled in the art, upon consideration of the present disclosure, may make modifications and/or improvements on this invention and still be within the scope and spirit of this invention as set forth in the following claims.

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#### WHAT IS CLAIMED IS:

1. A high molecular weight, high density
5 polyethylene polymer (HMW-HDPE) which has the following
physical properties:

molecular weight range of about 450,000 to 650,000,

- density range of from about 0.941 to 0.950, and melt index of about 0.5 g/10 min.
- 2. A method of producing a high molecular weight, 15 high density polyethylene polymer (HMW-HDPE) having the following physical properties:

molecular weight range of about 450,000 to 650,000,

- density range of from about 0.941 to 0.950, and melt index of about 0.5 g/10 min.;
- which method comprises the steps of mixing from about
  10 to 90 percent by weight of a high molecular weight
  high density polyethylene polymer with from 10 to 90
  percent by weight of a high molecular weight low
  density polyethylene polymer, and extruding the mixed
  materials to form the polymer having the recited
  physical properties.
  - 3. The method of Claim 2, wherein the mixing is conducted by physically blending the solid HMW-HDPE polymer and the solid HMW-LDPE, to form a solid

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admixture which is then extruded.

4. The method of Claim 2, wherein the mixing is conducted by physically compounding the solid HMW-HDPE polymer and the solid HMW-LDPE, to form a melted admixture which is then extruded.

5. Thin films produced from the polymer of Claim 1 having the following physical properties:

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- (a) Low haze (i.e., high clarity); the percentage of haze is less than about 50 percent, as measured by ASTM D-1003;
- (b) High Gloss (45°); the 45° gloss values are at least about 20, as measured by ASTM D-2457;
  - (c) High Light Transmission; the percentage of light transmission is at least about 85 percent, as measured by ASTM D-1003;
    - (d) Variation of Moisture Vapor Transmission; the films show variation in moisture vapor transmission (MVTR) values when compared to conventional HMW-HDPE polymer films as measured using ASTM F-372;
- (e) Increased Nitrogen Gas Permeation; the films show an increase in N<sub>2</sub> gas permeation values when compared to conventional HMW-HDPE polymer films ranging from about 1.5% up to about 17.2% as measured using ASTM D-3985;

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- (f) Increased Oxygen Gas Permeation; the films show an increase in O2 gas permeation values when compared to conventional HMW-HDPE polymer films ranging from about 3% up to about 22% as measured using ASTM D-3985; and
- (g) Low Coefficient of Friction; the films have a low coefficient of friction as measured using ASTM D-1894.
- 6. The thin films of Claim 5, which have the following physical properties:
- (aa) Low haze (i.e., high clarity); the percentage of haze is less than about 35 percent, as measured by ASTM D-1003;
- (bb) High Gloss (45°); the 45° gloss
  values of the films are at least about 30, as
  measured by ASTM D-2457; and
  - (cc) High Light Transmission; the percentage of light transmission is at least about 90 percent, as measured by ASTM D-1003.
  - 7. The thin films of Claim 5, which have the following physical properties:
- (aaa) Low haze (i.e., high clarity); the percentage of haze is less than about 20 percent, as measured by ASTM D-1003; and
  - (bbb) High Gloss (45°); the 45° gloss values of the films are at least about

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#### 40, as measured by ASTM D-2457.

8. A film of Claim 5, which is prepared by extruding a physical blend of from about 90% to about 10% by weight of a high molecular weight high density polyethylene (HMW-HDPE) and from about 10% to about 90% by weight of a high molecular weight low density polyethylene (HMW-LDPE) at a blow-up ratio ranging from about 4:1 to about 5:1.

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- 9. The film of Claim 8, wherein the physical blend of polymers is a blend of polymer solids.
- 10. The film of Claim 8, wherein the physical blend of polymers is a melt blend.
  - 11. The film of Claim 8, 9, or 10, wherein the HMW-HDPE is present in the blend at from about 80% to about 50% by weight.

- 12. The film of Claim 8, 9, or 10, wherein the HMW-HDPE is present in the blend at from about 80% to about 70% by weight.
- 25 13. Clear bags having exceptional strength, high sheen, and better transparency than conventional HDPE film based bags, prepared from the films of Claim 5, 6, 7, 8, 9, 10, 11 or 12.
- 14. A method of improving the haze properties of clear plastic films prepared from high molecular weight high density polyethylene (HMW-HDPE) resins, which method comprises adding a haze reducing amount of a high molecular weight low density polyethylene

(HMW-LDPE) resin to said HMW-HDPE resins and forming films from the blended and extruded resin mixture.

- 15. The method of Claim 14, wherein the blending of the polymers is conducted by admixing the individual solid polymer species.
- of the polymers is conducted by melt-mixing the individual polymer species.
  - 18. The method of Claim 14, 15, or 16, wherein the haze reducing amount of the HMW-LDPE is from about 10% to about 90% by weight.
  - 19. The method of Claim 14, 15, or 16, wherein the haze reducing amount of the HMW-LDPE is from about 20% to about 50% by weight.
- 20. The method of Claim 14, 15, or 16, wherein the haze reducing amount of HMW-LDPE is from about 20% to about 30% by weight.

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### INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/02557

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>6</sup>									
According to International Patent Classification (IPC) or to both National Classification and IPC									
1PC (3): CUBL 23/UG; CUGJ 3/16									
U.S. CL.: 525/240									
II. FIELDS SEARCHED									
Classification	- C	Minimum Docume	entation Searched 7						
Classification	on System	Classification Symbols							
U.S.									
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>									
III. DOCU	MENTS C	ONSIDERED TO BE RELEVANT 9							
Category *		on of Document, 11 with indication, where ap	propriate, of the relevant passages 12	Relevant to Claim No. 13					
$\frac{X}{Y}$	US,	A, 3,231,636 (SNYDER	) 25 January 1966	1-4					
Y	See	e.g. column 2, Table I.		5-12 and 14-20					
Х	US, See	1-12 and 14-20							
Х		A, 3,998,914 (LILLIS) 21 e.g. the Abstract and col	1-12 and 14-20						
Х	US, See	1-12 and 14-20							
"A" doc	ument defii	s of cited documents: 10 hing the general state of the art which is not be of particular relevance	"T" later document published after or priority date and not in confi cited to understand the princip	ict with the application but					
"E" earl	ier docume	nt but published on or after the international	invention " "X" document of particular relevan	ice: the claimed invention					
tiin	tiling date cannot be considered have or cannot be considered to								
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other concessions are of the concession of									
citation or other special reason (as specified)  Cannot be considered to involve an inventive step when the document referring to an oral disclosure, use, exhibition or document is combined with one or more other such docu-									
- Dini	other means ments, such combination being obvious to a person skilled								
"P" document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family									
IV. CERTIFICATION									
Date of the Actual Completion of the International Search  Date of Mailing of this International Search Report									
26 Ma	26 May 1992								
Internation	al Searchin	g Authority	Signature of Authorized Officer	1					
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Form PCT/ISA/210 (second sheet) (Rev.11-87)

# X-Rite, Incorporated

3100 44th St SW, Grandville, MI 49418

Telephone: 616-257-2319 Fax: 888-537-8402

February 7, 2006

Attn: Credit Department

DOW CHEMICAL CO.

FAX: 248-391-6417

Dear Sir or Madam,

So that we may consider establishing an open account for a line of credit for the company listed below, we would appreciate the following information:

Name:

CONTINENTAL PLASTICS CO.

Address:

33525 GROESBECK HIGHWAY

City, State, Zip

**FRASER, MI 48026** 

Phone:

586-294-4600 Account:

Date account opened:		Terms:				
Credit Limit Established:		Recent High Credit:				
Current Total Outstanding:		Amount Past Due:				
Please indicate manner of pa	yment customer has	nandled their account:				
( )Discounts ( )Slow To 30 Days	( ) prompt ( )60 Days	( )Pays On				

Type of product supplied to customer:

Last sale date:

Credit refused (please state reason why):

Date:\_\_\_\_\_\_

Please return this inquiry via fax to (888) 537-8402 or (616) 534-0572.

Signature & Title:

Thank you in advance for your prompt response. All information will be held in s ict confidence.

Sincerely,

on behalf of X-Rite, Inc.

CONNIE HUSTON

Credit Assistant